the metal loadings are carried out with different methods, is there any difference in the activity ?

Obviously the catalyst of 1.0% Pt-2.0% Co/ZSM-5 shows higher activity in higher CO conversion than that of 1.0% Pt-2.0% Cu/ZSM-5 and 1.0% Pt/ZSM-5. With 1.0% Pt-2.0% Co/ZSM-5i, 100% CO oxidation was obtained at 180 ℃ , while for 1.0% Pt/ZSM-5i and 1.0% Pt-2.0% Cu/ZSM-5i complete conversion was observed at 180 ℃ and 190 ℃ , respectively.

It is interesting to note that the activity depends on the loading method of metals into supports. High temperature solid-state reaction is an alternative mean of transition metal ion introduced into zeolites or molecular sieves.[15] The catalyst of 1.0% Pt-2.0% Co/ZSM-5s shows much higher activity than 1.0% Pt/ZSM-5i&s by 20-25, 30-35 and 90% at 100, 120, and 140 ℃ , respectively. On the other hand the activity of 1.0% Pt-2.0% Cu/ZSM-5s catalyst shows higher than 1.0% Pt-2.0% Cu/ZSM-5i by about 10% beyond 140 ℃ . However the activity of 1.0% Pt/ZSM-5s is lower than 1.0% Pt/ZSM-5i. There is no evidence that 1.0% Pt-2.0% Cu/ZSM-5 reveals higher activity than 1.0% Pt/ZSM-5.

Liao *et al.*[16] also has reported that there was no improvement of catalytic activity on CO oxidation for Pt-Cu/γ-Al$_2$O$_3$, where Pt and Cu were loaded by co-impregnation of γ-Al$_2$O$_3$ with salt solutions of Pt and Cu.

The relative catalytic activity of various catalysts for CO oxidation is summarized and compared in Table 1. Pure HZSM-5 without promoters shows very low activity for CO oxidation. Other promoters such as Ga, Mo, Fe and Cu+Co do not show higher activities than Co, Cu and Pt.

In order to understand the behavior of bimetallic catalysts, Pt-Co/ZSM-5 with different metallic concentrations have been investigated by X-ray diffraction. However ZSM-5 supported catalysts could not be examined due to the interference between the metal and the support.

Dees and Ponec[17] observed partial alloy formation of Pt/Co on silica-supported catalysts with XRD evidence. This alloy formation seems to improve the CO oxidation performance than any other active metals studied in this work.

There is only a few reports on the CO oxidation with Pt-Cu and Pt-Co dispersed on the support.[16,18] Similar work is currently under study by the authors.

Generally it's desirable for catalysts to maintain high activity without significant decay in performance. In order to measure water vapor effect, water vapor was supplied *via* by-pass route to feed gases as necessary, prior to their reach of the reactor. From our limited study for CO oxidation, Pt-Co catalyst showed higher activity than others. For 1.0% Pt-2.0% Co/ZSM-5, it was observed that CO oxidation activity in the presence of water vapor were almost identical to that in the absence of water vapor within ± 6%, while 100% conversion temperature was the same each other, and the overall activity was retained at least 300 min even in the presence of water vapor.

Conclusively the catalyst of 1.0% Pt-2.0% Co/ZSM-5s is the most active catalyst for CO oxidation examined thus far in this work. The selection of the most active transition metals as well as the addition of the noble metals are efficient in improving the active catalytic activity for CO oxidation. It is also found that for the loading of metal ions high temperature solid-state reaction method is more effective than the ion-exchange followed by impregnation method.

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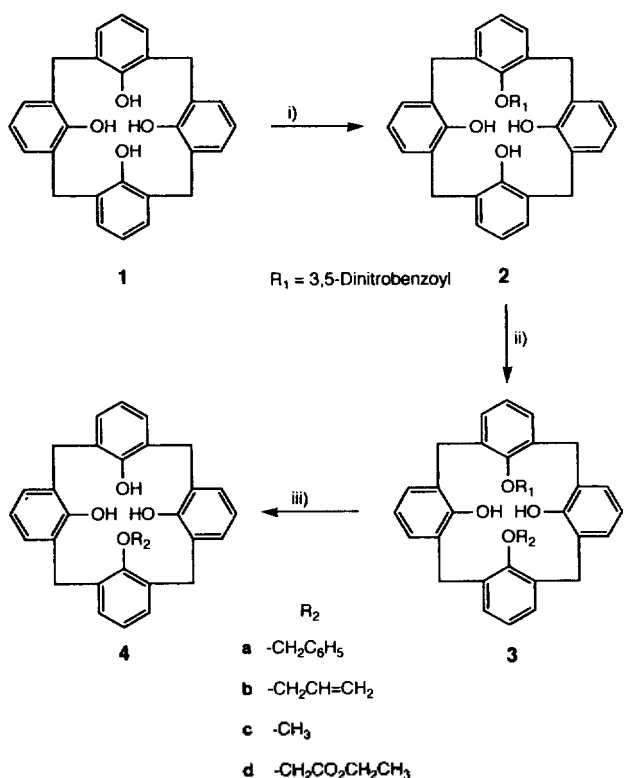19. Shelef, M.; Otto, K.; Gandhi, H. *J. Catal.* 1968, *12*, 361.

Monoalkylation of Calix[4]arene

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Selective functionalization of calixarene has greatly widened the use of calixarenes in Host-Guest chemistry. Several synthetic procedures have been reported that alkylated the calix[4]arene selectively such as the 1,3-dialkylation,[1,2] 1,2-dialkylation,[3] and trialkylation[4] at the lower rim of calix[4] arene. Utilizing the selective functionalization at the lower rim of calix[4]arene, the monoalkylated calix[4]arenes

Notes

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1

R₁ = 3,5-Dinitrobenzoyl   2

4

a -CH₂C₆H₅
b -CH₂CH=CH₂
c -CH₃
d -CH₂CO₂CH₂CH₃

3

Scheme 1.

which were used for the synthesis of chiral calixarenes[5] have been prepared by the three step method utilizing either selective functionalization such as tribenzoylation, monoallylation followed by hydrolysis of benzoyl groups[6] or selective cleavage[7] of tetraalkyl calix[4]arene with iodotrimethyl silane. Also Reinhoudt and Ungaro reported the synthesis of monoalkylated calix[4]arenes *via* direct alkylation method.[8] In this paper we report the another efficient three step method for the synthesis of the monoalkylated calix[4]arenes.

p-tert-Butylcalix[4]arene was reported to react with 3,5-dinitrobenzoyl chloride to produce the monobenzoylated calix [4]arene.[9] We found that under the same reaction conditions calix[4]arene 1 also reacted with 3,5-dinitrobenzoyl chloride to give the mono-3,5-dinitrobenzoylated calix[4]arene 2. Calix[4]arene 1 which can be functionalized at the lower rim as well as at the upper rim might be a more useful starting material than *p-tert*-butylcalix[4]arene for the preparation of chiral calixarenes. Assuming that the bulkiness of 3,5-dinitrobenzoyl group at the lower rim of calix[4]arene could control the second substitution at the lower rim we carried out the alkylation of 2 with various alkyl halides in the presence of base. Treatment of 2 with excess benzyl bromide in the presence of 3 equivalents of K₂CO₃ produced the disubstituted calix[4]arene 3a in 88% yield. When pyridine was used as a base for the etherification of 2, the reaction was not occurred at all even under the vigorous conditions. Allyl bromide, methyl iodide as well as ethyl bromoacetate also reacted with 2 to yield the corresponding 3b, 3c, and 3d in high yield as shown in Scheme 1. The ¹H NMR spectrum of 3a showed two pair of doublets at 3.20-4.10 ppm arising from the bridging methylene protons and a singlet at 5.40 ppm for the two hydroxy protons, indicating that the second subs-

titution was occurred at the opposite side of lower rim of 2 and the conformation of 3a is cone. The ¹H NMR spectra of 3b, and 3d showed the same characteristic features described for 3a, that is, two pair of doublets for the methylene protons and one singlet for hydroxy protons. But the ¹H NMR spectrum of 3c indicated that 3c is in a different type conformation compared with 3a, 3b, and 3d. For the bridge methylene protons four pair of doublets showed up at the 3.30-4.20 ppm. The remaining peaks such as a singlet at 3.82 ppm for the methoxy resonance and aromatic peaks at 5.80-7.70 indicate that the only monomethylation was occurred. Monomethylation was confirmed by the base hydrolysis of 3c. Therefore, it is certain that reaction of 2 with methyl iodide in the presence of K₂CO₃ produced the monomethylated calix[4] arene 3c. But the conformation of 3c is not cone as observed for 3a, 3b, and 3d, but either partial cone conformation with one hydroxy group down or 1,2-alternate based on the observed ¹H NMR spectrum assuming that 1,3-opposite side disubstitution was occurred. X-ray crystallography could reveal the conformation clearly but are not available at this moment. The ¹³C NMR spectrum of 3c confirmed the same conformation, which showed four peaks at 31.12, 31.47, 37.41 and 37.89 ppm for the four bridge methylene carbons and one peak at 61.21 ppm for the one methoxy carbon and the very complicated aromatic peaks.

The monoalkylated calix[4]arenes 4a, 4b, 4c, and 4d were obtained easily by the base hydrolysis[10] of corresponding ester 3a, 3b, 3c, and 3d as shown Scheme 1. 3,5-Dinirobenzoyl group of 3a and 3c was removed with NaOH in THF-EtOH-H₂O solution under reflux. When 3b was treated with NaOH under reflux, some of allyl groups rearranged to the *para* position. But when the reaction temperature was lowered to room temperature, none of the product was rearranged. Hydrolysis of 3d under the base conditions could be subtle. Compound 3d was treated with sodium ethoxide to prevent ester hydrolysis, but failed. 3,5-Dinitrobenzoyl group as well as ester group were hydrolyzed to yield the acid of 4d.

The ¹H NMR spectrum of 4a showed the two singlets at 9.69 and 9.34 ppm at the ratio of 1:2 arising from the 3 hydroxy protons, the multiplet at 6.67-7.09 arising from the 17 aromatic protons, a singlet at 4, 14 ppm arising from the two benzyl protons, and two pair of doublets at 3.44-4.38 arising from the 8 bridge methylene protons consistent with the cone conformation of the monobenzylcalix[4] arene 4a. The ¹H NMR spectra of 4b, 4c, and 4d also showed the similar spectral patterns described above such as two singlets for the 3 hydroxy protons and two pair of doublets for the 8 bridge methylene protons, indicating that the conformation of 4b, 4c, and 4d also is cone.

Experimental

Melting points of all compounds were measured on a Mel-Temp apparatus without calibration. Infrared (IR) spectra were determined on a Nicolet 520 FT-IR spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 300 AMX spectrometer. Chemical shifts are reported as δ values in parts per million relative to tetramethylsilane as an internal sta.... Thin layer chromatography (TLC) analyses were carried out on silica gel plates.

25-(3,5-Dinitrobenzoyloxy)-26,27,28-trihydroxycalix

[4]arene (2). To a solution of 1.6 g (3.9 mmol) of **1b** in 40 mL of acetonitrile 4.8 mL of 1-methyl imidazole and 1.2 g of 3,5-dinitrobenzoyl chloride (5.2 mmol) was added. The mixture was stirred at room temperature for 6 h. acidified, and extracted with $CHCl_3$. After removed the solvents, the residue was triturated with methanol. The crude product was recrystallized from $CHCl_3$-MeOH to yield 1.47 g (63%) of pale yellow crystalline **2**: mp 288 °C dec., ^{1}H NMR ($CDCl_3$) 9.11 and 8.10 (two d, 3H, O_2NArH, $J=2.2$ Hz), 6.16-7.61 (m, 12H, ArH), 3.60-4.02 (two pair of d, 8H, $ArCH_2Ar$, $J=14.2$); ^{13}C NMR ($DMSO$-d_6) 162.08 (-CO_2-), 156.49, 153.95, 148.47, 144.91, 136.44, 133.31, 132.74, 130.12, 129.69, 129.38, 129.33, 128.23, 128.15, 127.86, 127.51, 125.75, 122.88, 122.83, 122.05, 118.05, and 116.00 (Ar), 33.00 and 32.05 (-CH_2-); IR (KBr) 3450 cm^{-1} (OH), 1730 cm^{-1} (-CO_2-).

25-(3,5-Dinitrobenzoyloxy)-27-(benzyloxy)-26,28-dihydroxycalix[4]arene (3a). To a solution of 0.5 g (0.8 mmol) of **2**, 0.34 g (2.4 mmol) of K_2CO_3 and 1.92 mL (16 mmol) of benzyl bromide in 50 mL of THF was added and refluxed for 1.5 h. The solvents were evaporated and the residue was dissolved with 30 mL of $CHCl_3$ and washed with 0.1 N HCl. The organic layer was separated, dried over Na_2SO_4, evaporated the solvents, and the residue triturated with MeOH. Recrystallization of crude product yielded 0.35 g (65 %) of pale yellow **3a**: mp 267-270 °C. ^{1}H NMR ($CDCl_3$) 9.70 and 9.33 (two d, 3H, O_2NArH, $J=2.2$ Hz), 6.65-7.38 (m, 17H, ArH), 6.95 (s, 2H, OH), 5.40 (s, 2H, OCH_2Ar), 3.48-4.05 (two pair of d, 8H, $ArCH_2Ar$, $J=13.92$ and 13.19 Hz); ^{13}C NMR ($CDCl_3$) 161.73 (-CO_2-), 152.61, 149.59, 148.81, 144.99, 134.21, 133.99, 132.91, 131.88, 130.57, 130.06, 129.85, 129.39, 128.89, 128.75, 128.70, 128.48, 126.69, 126.29, 122.65, and 119.68 (Ar), 80.29 (-OCH_2-), 31.79 (-CH_2-); IR (KBr) 3446 cm^{-1} (OH), 1740 cm^{-1} (-CO_2-).

25-(3,5-Dinitrobenzoyloxy)-27-allyloxy-26,28-dihydroxycalix[4]arene (3b). A mixture of 1.0 g of **2**, 0.68 g of K_2CO_3 and 4.1 mL of allyl bromide in 50 mL of THF was refluxed for 2.5 h and followed the procedure described for **3a** to yield 0.8 g (76%) of pale yellow **3b** after recrystallization from $CHCl_3$-MeOH. mp 209-212 °C ^{1}H NMR ($CDCl_3$) 9.65 and 9.30 (two s, 3H, O_2N ArH), 6.70-7.10 (m, 14H, ArH), 6.30 (m, 1H, -CH=), 5.50 and 5.38 (m, 2H, =CH_2), 4.78 (d, 2H, -CH_2- from allyl methylene, $J=6.6$ Hz), 3.40-4.10 (two pair of d, 8H, $ArCH_2Ar$, $J=13.92$ and 13.19 Hz); ^{13}C NMR ($CDCl_3$) 161.84 (-CO_2-) 152.67, 150.13, 148.90, 145.15, 134.10, 132.63, 131.96, 131.37, 130.49, 129.87, 128.97, 128.72, 128.56, 126.80, 126.34, 126.13, 122.65, 121.04 and 119.71 (from aromatic and vinyl carbons), 79.03 (-OCH_2-), 32.14 and 31.82 ($ArCH_2Ar$); IR (KBr) 3400 cm^{-1} (OH), 1740 cm^{-1} (-CO_2-).

25-(3,5-Dinitrobenzoyloxy)-27-methyloxy-26,28-dihydroxycalix[4]arene (3c). A mixture of 0.5 g (0.8 mmol) of **2**, 0.34 g of K_2CO_3 and 0.23 mL of CH_3I in 50 mL of THF was refluxed for 15 h and followed the procedure described for **3a** to yield 0.28 g (54%) of pale yellow crystalline **3c** after recrystallization from toluene. mp 285 °C dec. ^{1}H NMR ($CDCl_3$) 8.95, 8.20 and 7.60 (three s, 5H, O_2NArH and OH), 6.22-7.48 (m, 12H, ArH), 3.38-4.20 (four pair of d, 8H, $ArCH_2Ar$, $J=13.20$ Hz), 3.82 (s, 3H, -OCH_3). ^{13}C NMR ($CDCl_3$) 159.48 (-CO_2-), 152.02, 150.74, 147.69, 147.05, 134.85, 133.51, 132.79, 132.17, 131.67, 130.81, 129.93, 129.74, 129.61, 129.39, 129.10, 128.89, 128.62, 128.51, 128.06, 127.52, 126.64, 125.43, 124.69, 122.01, 121.50 and 119.60 (ArH), 61.21 (-OCH_3), 37.89,

37.41, 31.47, 31.12 ($ArCH_2Ar$); IR (KBr) 3300 cm^{-1} (OH), 1738 cm^{-1} (-CO_2-).

25-(3,5-Dinitrobenzoyloxy)-27-ethoxycarbonylmethoxy-26,28-dihydroxycalix[4]arene (3d). A mixture of 0.5 g of **2** and 0.9 mL of ethyl bromoacetate in 50 mL of THF in the presence of 0.34 g of K_2CO_3 was refluxed for 2.5 h and followed the procedure described for **3a** to yield 0.35 g (62%) of pale yellow crystalline **3d** after recrystallization from $CHCl_3$-MeOH. mp 265 °C dec. ^{1}H NMR ($CDCl_3$) 9.74 and 9.28 (two s, 3H, O_2NArH), 7.11-6.66 (m, 12H, ArH), 7.25 (s, 2H, OH), 4.82 (s, 2H, -OCH_2-), 4.14-3.38 (pair of d, 8H, $ArCH_2Ar$), 4.20 (q, 2H, -CH_2-), 1.31 (t, 3H, -CH_3). ^{13}C NMR ($CDCl_3$) 169.44 (-CO_2-), 153.14, 151.70, 149.25, 145.00, 134.60, 133.02, 132.65, 131.35, 130.40, 129.42, 129.24, 128.88, 127.66, 126.86, 126.21, 122.88, and 120.13 (Ar), 73.19 and 62.47 (two -OCH_2-), 32.43 and 32.33 ($ArCH_2Ar$).

25-Benzyloxy-26,27,28-trihydroxycalix[4]arene (4a). A mixture of 1.11 g (1.57 mmol) of **3a**, and 1.5 g of NaOH in 100 mL THF, 30 mL EtOH and 60 mL of H_2O was refluxed for 1 h. Acidified and extracted with $CHCl_3$, evaporated the solvents, and the crude product was recrystallized from $CHCl_3$-MeOH to yield 0.54 g (68%) of white plate **4a**: mp 224-225 °C (lit.[7] 225-226 °C). ^{1}H NMR ($CDCl_3$) 9.69 and 9.34 (two s, 3H, OH), 6.67-7.09 (m, 17H, ArH), 3.44-4.38 (two pair of d, 8H, $ArCH_2Ar$); ^{13}C NMR ($CDCl_3$); 151.08, 149.67, 134.49, 129.82, 129.25, 129.14, 128.99, 128.85, 126.63, 122.31, and 121.41 (Ar), 63.90 (-OCH_3), 32.30 and 31.72 ($ArCH_2Ar$). IR (KBr) 3280 cm^{-1} (OH).

25-Allyloxy-25,26,27-trihydroxycalix[4]arene (4b). A mixture of 0.5 g of **3b** and 0.4 g of NaOH in 40 mL THF, 10 mL EtOH and 15 mL of H_2O was stirred for 1 h and work up as described for **4a** to give 0.25 g (70%) of **4b**. mp 216-217 °C (lit.[7] 216-217 °C). ^{1}H NMR ($CDCl_3$) 9.60 and 9.25 (two s, 3H, OH), 7.50-6.50 (m, 12H, ArH), 6.0-6.5 (m, 1H, -CH=), 5.4-5.9 (m, 2H, =CH_2), 4.6-4.8 (d, 2H, -OCH_2-), 3.3-4.5 (two pair of d, 8H, $ArCH_2Ar$); ^{13}C NMR ($CDCl_3$) 151.22, 150.75, 149.27, 134.32, 132.26, 129.37, 128.98, 128.83, 128.78, 128.76, 128.48, 128.40, 128.25, 126.25, 121.92, 120.96, and 120.32 (Ar). 77.72 (-OCH_2-), 31.90 and 31.70 ($ArCH_2Ar$). IR (KBr) 3300 cm^{-1} (OH).

25-Methoxy-25,26,27-trihydroxycalix[4]arene (4c). Following the procedure described for **4a**, 0.20 g (60%) of **4c** was obtained. mp 276-277 °C (lit.[7] 276-277 °C). ^{1}H NMR ($CDCl_3$) 9.70 and 9.35 (two s, 3H, OH), 6.7-7.1 (m, 12H, ArH), 4.27-4.37 (two pair of d, 8H, $ArCH_2Ar$), 4.13 (s, 3H, -OCH_3); ^{13}C NMR ($CDCl_3$) 153.21, 151.10, 149.68, 134.51, 129.84, 129.27, 129.16, 129.00, 128.87, 128.85, 126.64, 122.33, and 121.43 (Ar), 63.89 (-OCH_3), 31.32 and 31.74 ($ArCH_2Ar$). IR (KBr) 3340 cm^{-1} (OH).

25-Carboxymethoxy-26,27,28-trihydroxycalix[4] arene (acid of 4d). A mixture of 0.176 g of **3d** in 20 mL of THF and 15 mmole of sodium ethoxide prepared 0.35 g of sodium in 10 mL of ethanol was refluxed for 17 h. Following the procedure described for **4a** to obtain 0.09 g (75%) of acid of **4d**. mp 136-138 °C (dec). ^{1}H NMR ($CDCl_3$) 6.67-7.47 (m, 12H, ArH), 4.85 (s, 2H,-CH_2O-), 3.52-4.44 (two pair of d, $ArCH_2Ar$). IR (KBr) 3320 cm^{-1} (OH), 1742 cm^{-1} (-CO_2-).

Notes

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Convenient Synthesis of Symmetrical Sulfides from Alkyl Halides and Epoxides

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Received October 31, 1994

Sometime ago symmetrical sulfides were reported to be prepared in excellent yields from alkyl halides and sodium sulfide in water in the presence of a phase-transfer catalyst (PTC)[1] or polymer supported phase-transfer catalyst.[2] Primary alkyl chlorides and secondary alkyl bromides reacted a little slower than primary bromides, but not with much difference. Bis(tributyltin) sulfide was also reported to give excellent yields of symmetrical sulfides, but require longer reaction time (12 h) at elevated temperature (110 °C).[3] Recently we have observed the synthesis of phenyl sulfides is facilitated by the presence of an anion exchange resin,[4] and also showed good chemoselectivity: primary bromides reacted selectively in the presence of primary chlorides and secondary bromides. We anticipated the presence of a catalytic amount of a commercial anion exchange resin[5] in the synthesis of symmertrical sulfides from alkyl halides and sodium sulfide might also show a good chemoselectivity, rate acceleration and simplification of work-up procedure as we observed in the synthesis of phenyl sulfides.[4] We tested the possibility, and have found a convenient synthetic procedure for symmetrical sulfides.

As shown in Table 1, octyl bromide, iodide and tosylate

Table 1. Synthesis of Symmetrical Sulfides from Alkyl Halides and Epoxides using Sodium Sulfide in the Presence of Amberlite IRA-400 in Methanol[a]

Entry	Substrate	Time (h)	Product	Yield[b]
1	octyl chloride	12	dioctyl sulfide	95[c]
2	octyl bromide	1	dioctyl sulfide	95
3	octyl iodide	1	dioctyl sulfide	96
4	octyl tosylate	1	dioctyl sulfide	94
5	neopentyl bromide	6	dineopentyl sulfide	0
6	benzyl chloride	1	dibenzyl sulfide	96
7	benzyl bromide	1	dibenzyl sulfide	95
8	cinnamyl chloride	1	dicinnamyl sulfide	90
9	2-hexyl bromide	6	di-2-hexyl sulfide	(65)[d]
10	2-octyl tosylate	6	di-2-octyl sulfide	(72)
11	cyclohexyl bromide	6	dicyclohexyl sulfide	0
12	1-bromo-4-chloro-butane	1	tetrahydrothiophene	(97)
13	1,2-dibromooctane	1	1,2-octene episulfide	95[c]
14	1,2-decene oxide	1	di-β-hydroxydecyl sulfide	92
15	cyclohexene oxide	1	di-β-hydroxycyclohexyl sulfide	96

[a] Reactions were carried out with 0.55 eq of Na_2S in the presence of 0.1 eq of Amberlite IRA-400 under reflux in methanol. [b] Isolated yields. GC yields were in parenthesis. [c] With 1 eq of Amberlite. [d] With 0.7 eq of Na_2S. [e] With 1.1 eq of Na_2S and 0.2 eq of Amberlite.

reacted rapidly with stoichiometric amount of sodium sulfide (0.55 eq) in methanol giving the corresponding symmetrical sulfides quantitatively in 1 h at 65 °C in the presence of 0.1 eq of Amberlite (entries 2, 3 and 4). However octyl bromide required 9 h in the absence of the resin showing the catalytic activity of anion exchange resin. Octyl chloride reacted even more slowly showing only 20% progress of the reaction in 1 h and 60% in 24 h, however quantitative yield of dioctyl sulfide could be obtained in 12 h using 1 eq of Amberlite (entry 1). Benzyl and cinnamyl halides also gave the corresponding sulfides quantitatively even at room temperature (entries 6, 7 and 8). On the other hand, the reaction with 2-hexyl bromide and 2-octyl tosylate proceeded slowly accompanying elimination and gave only moderate yields of di-2-hexyl sulfide (65%) and di-2-octyl sulfide (72%) (entries 9 and 10). However neopentyl bromide and cyclohexyl bromide, more hindered halides, did not react at all in 6 h (entries 5 and 11). 1-Bromo-4-chlorobutane reacted readily but gave tetrahydrothiophene instead of expected di-4-chlorobutyl sulfide (entry 12). Presumably 4-chlorobutyl sulfide anion, the initially formed intermediate, reacted intramolecularly rather than intermolecularly. Similarly 1,2-dibromooctane gave 1,2-octene episulfide quantitatively instead of di-2-bromooctyl sulfide (entry 13). Since vicinal dibromo compounds are readily prepared from the corresponding alkenes, this could be a convenient alternative synthetic method of thiiranes, valuable intermediates in organic synthesis.[6] Finally both 1,2-decene oxide and cyclohexene oxide gave the corresponding di-β-hydroxy sulfides in excellent yields (ent-